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## Production of carbon nanotubes (CNTs) from thermochemical conversion of waste plastics using Ni/anodic aluminum oxide (AAO) template catalyst

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### Abstract

In this work, the production of carbon nanotubes (CNTs) from waste plastics was investigated to reduce the cost of CNTs production, as well as providing alternative management for waste plastics. A template-based catalyst (Ni/anodic aluminum oxide–AAO) was studied herein to control the growth of CNTs with uniform distribution of diameters. The addition of a conditioning catalyst (for modifying carbon sources) was studied for their influences on the formation of CNTs on Ni/AAO. A two-stage reactor was used to test the prepared catalysts which were also characterized with various methods e.g. scanning electronic microscopy (SEM) and temperature programmed oxidation (TPO). The results show that the introduction of a conditioning catalyst (Ni/Al<sub>2</sub>O<sub>3</sub>) positively affected the growth of CNTs with more uniform distribution of diameters of CNTs.

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**Keywords:** Plastics waste; Carbon nanotubes; AAO membrane; Nickel; Catalyst

### 1. Introduction

Converting waste plastics into CNTs and hydrogen-enriched gases is a promising alternative method to manage waste plastics. Recently, co-production of carbon nanotubes (CNTs) from pyrolysis/gasification of waste plastics is widely studied [1, 2]. However, CNTs produced from catalytic thermal-chemical conversion of waste plastics are

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normally of poor quality due to the use of granular catalyst e.g. Ni/Al<sub>2</sub>O<sub>3</sub>. The quality of carbon nanotubes is suggested to be related to the distribution of diameters, length and wall thickness [3].

In order to produce CNTs with controlled uniform diameters, a template-based synthesis has been introduced. Ni-coated glass was successfully used as a template by Ren et al. [1] to synthesise ordered CNTs from acetylene at above 700 °C using plasma-enhanced hot filament CVD method. Che et al. [2] prepared graphitic carbon nanotubes within a porous alumina template from ethylene and pyrene using a CVD method in the presence of a Ni-based catalyst. This template method provides a support with uniform structure for the growth of CNTs. Anodic aluminium oxide (AAO) membrane has been widely used as a template for CNTs growth using pure carbon source. AAO membrane presents several features, such as achievable pore diameter, lengths and inner pore distances. These features lead to the production of CNTs with a high morphological quality, and also because of the fact that AAO could be easily dissolved in alkaline or acidic solutions during the separation of CNTs [4].

Most studies focused on the production of CNTs on AAO based catalyst from pure hydrocarbon sources. For example, Chen et al. [5] synthesized CNTs by casting thin films of polyacrylonitrile and polystyrene-block-polyacrylonitrile within AAO membrane followed by pyrolysis. They found that the wall thickness of the produced CNTs was controlled by the concentration of the precursor solution. The effect of reaction gases (CO and C<sub>2</sub>H<sub>2</sub>) on the formation of CNTs has been studied by Jeong et al. [6] with a Co-based AAO catalyst. CNTs synthesized in the presence of CO showed a lower growth rate when compared to C<sub>2</sub>H<sub>2</sub>. There are only few reports using waste plastics as a feedstock in the presence AAO template catalyst to synthesize CNTs. Therefore, in this work Ni-based AAO catalysts were investigated for the production of CNTs from pyrolysis/gasification of waste plastics aiming to generating high quality CNTs with uniform distributions. The influence of conditioning catalyst (used to modify hydrocarbon vapours derived from pyrolysis of plastic) was studied to optimize the process conditions.

## 2. Experimental

### 2.1 Materials preparation

Waste high density polyethylene (HDPE) plastics with a diameter about 2 mm were obtained from Poli Plastic Pellets Ltd. 10 wt.% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (conditioning catalyst) was synthesised by a wet-impregnation method. AAO membrane used in this study was from Whatman (Anodisc 13) with a 200 nm nominal pore diameter and a 60 µm thickness. First, the required amount of Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1 mol L<sup>-1</sup>) was dissolved in ethanol. Nickel precursor was doped on AAO by dropping the precursors on AAO. The obtained Ni/AAO membrane precursor was dried in an oven at 100 °C for 24h and then calcined in air at 700 °C with a 10 °C min<sup>-1</sup> heating rate for 3 hours. It is noted that the Ni/AAO catalysts prepared from using 0.1 mol L<sup>-1</sup> Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were assigned as 0.1AAO.

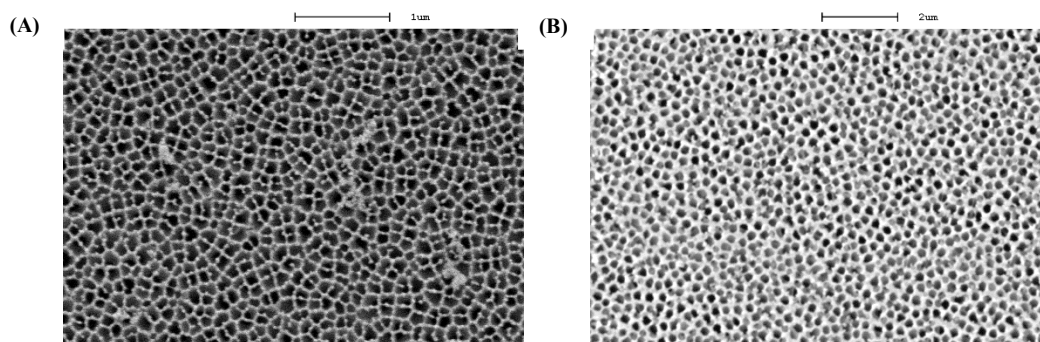
### 2.2 CNTs synthesis from catalytic thermal chemical of waste plastics

A two-stage catalytic thermal chemical conversion reaction was used in this study. In each experiment, about 1 g HDPE was pyrolysed at 500 °C in the first stage. The produced vapours representing a hydrocarbon source passed to the second reaction stage at 700 °C, where a conditioning layer of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (if used) and the Ni/AAO catalyst were located. The layer of conditioning catalyst was used to change the sources of hydrocarbons derived from the pyrolysis of waste plastics prior to the growth of CNTs on the Ni/AAO catalyst. N<sub>2</sub> was used as a carrier gas with 100 mLmin<sup>-1</sup> flow rate. The reacted Ni/AAO catalyst including the grown CNTs was collected for further characterizations. The effect of the introduction of the layer of Ni/Al<sub>2</sub>O<sub>3</sub> conditioning catalyst was studied in relation to their influences on growth of CNTs. It is to be noted that gaseous and liquid products were not analysed in this work, as the main aim was to investigate the growth of CNTs. More details about the reactor could be seen in previous work [7].

## 3. Results and discussions

### 3.1 Characterisations of fresh catalysts

Fig. 1 shows SEM (scanning electron microscopy) pictures of the fresh AAO membrane without Ni loading and the fresh 0.1AAO. EDX was studied to obtain the content of Ni, O and Al on the 0.1AAO, it shows that Ni content was 2.4 wt.%. Element of O was originated from NiO and AAO, and Al was from AAO. A large number of uniform pores and highly ordered nanochannels could be observed on the surface of the AAO membrane (Fig.1A) without nickel loading. The structure of the AAO used in this study is consistent with AAO templates used in other studies [6, 8, 9]. The surface of the 0.1AAO (Fig.1B) shows similar structure (many uniform pores) compared with the fresh AAO surface. It means the Ni catalyst was loaded inside the AAO pores instead of accumulating on the surface.



**Fig.1.** SEM results of fresh AAO membrane (A); and fresh 0.1AAO (with Ni loading) catalyst (B).

### 3.2 Influence of the addition of conditioning catalyst on CNTs formation

A layer of conditioning Ni/Al<sub>2</sub>O<sub>3</sub> (0 g, 0.2 g, 0.5 g, and 1 g) catalyst was placed on the top of the 0.1AAO to form CNTs through catalytic thermal chemical conversion of waste plastics at 700 °C. The aim was to investigate the influence of the modification of carbon sources on the production of CNTs from waste plastics.

Tip-growth and base-growth are two models for the production of CNTs, according to the interaction between catalysts and substrate. When the catalyst-substrate interaction is weak, hydrocarbon sources decompose on the top surface of the catalyst metal, carbon diffuses through catalytic particles. And CNTs are formed across the bottom of metal particles, pushing the catalyst particle off the substrate. When the catalyst-substrate interaction is strong, initial hydrocarbon decomposition and carbon diffusion take place similar to that in the tip-growth model, but the catalyst particle remains at the bottom of the substrate.

Filamentous carbons were observed on the surface of the catalyst. Fig. 2(A) shows the CNTs produced without the conditioning catalyst. The pores of 0.1AAO could still be clearly observed, indicating that the surface was not covered with filamentous carbons. When 0.2 g conditioning catalyst was placed on the top of the AAO catalyst, the SEM results (Fig. 3(A)) show that a small amount of filamentous was obtained. When more conditioning catalysts (0.5 g and 1 g Ni/Al<sub>2</sub>O<sub>3</sub>) were used, more filamentous carbons could be observed on the surface of the 0.1AAO. TEM results (Figs. 3(i)-(iii)) further confirm that the filamentous carbons were mainly carbon nanotubes. The distribution of diameters of the CNTs produced using various amounts of conditioning catalysts was also investigated. Two or more peaks of diameter distribution were observed using 0 g (Fig. 2(b)) and 0.2 g (Fig. 3(a)) conditioning catalysts, indicating that non-uniform CNTs were produced under these conditions. When 0.5 g and 1.0 g of conditioning catalysts were used, the diameter distribution of the produced CNTs seems to be improved, as a small deviation (4 nm) of diameter was obtained. The quantity of CNTs was assessed by temperature programmed oxidation (TPO) analysis, and the TGA-TPO (weight loss data) and DTG-TPO (derivate data) results are shown in Figs. 4(A) and 4(B), respectively. It is suggested that similar pattern of carbon oxidation was observed from the TPO results, as one main oxidation peak at around 620 °C was found for all the AAO-based catalysts using various amounts of conditioning catalysts. However, the amount of carbon yield seems to be increased with the increase of the amount of conditioning catalyst. For example, the weight loss was increased from 4 to 9%, when the amount of conditioning catalyst was increased from 0 to 1 g.

According to the above mentioned results, it is found that the presence of the conditioning catalyst could enhance the production of CNTs. This is because the carbon sources responsible for the production of CNTs were modified

by the introduction of conditioning catalyst. It is known that the conditioning catalyst ( $\text{Ni}/\text{Al}_2\text{O}_3$ ) was effective to crack heavy hydrocarbons into small molecules during gasification process [10]. For example, Barbaties et al. [10] used a  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst to produce hydrogen from catalytic steam reforming of plastics (PS and HDPE).

The carbon source is one of the most important parameters for the synthesis of CNTs. A significant relationship between chemical structure of hydrocarbons and CNTs growth was reported by Lee et al. [11, 12]. They studied the effect of different carbon sources on the growth of CNTs using different catalysts (Ni, Co and Fe based). They reported that the growth rate of CNTs was much higher and the average diameter became smaller when the ratio of  $\text{NH}_3/\text{C}_3\text{H}_4$  was increased. The influence of six types of hydrocarbons (methane, hexane, cyclohexane, benzene, naphthalene and anthracene) on the production of single walled CNTs was investigated with a  $\text{Fe}/\text{MgO}$  catalyst [13]. Methane was found to be responsible for producing high-purity CNTs, because the Gibbs free energies of hexane, cyclohexane and benzene were much lower than methane. In addition, the influence of virgin

plastics and waste plastics on CNTs production were studied by Borsodi et al. [14]. In this work, the presence of a layer of conditioning catalyst ( $\text{Ni}/\text{Al}_2\text{O}_3$ ) on the top of the  $\text{Ni}/\text{AAO}$  catalyst was expected to modify the hydrocarbon sources derived from the pyrolysis of waste plastics. Hydrocarbon gaseous compounds produced from the pyrolysis of plastic waste were mainly large hydrocarbon molecules. These large compounds were cracked into smaller ones in the presence of the conditioning catalyst. It is suggested that smaller hydrocarbon molecules are beneficial for the growth of CNTs on the  $\text{Ni}/\text{AAO}$  catalyst. The effect of large hydrocarbon molecules on CNTs formation was also reported by Acomb et al [7]. They studied the formation CNTs from different types of plastic waste, and it was found that more CNTs could be produced from using low density polyethylene (LDPE) when compared with either polypropylene (PP) or polystyrene (PS). This is because larger hydrocarbon molecules produced from the pyrolysis of PP and PS could form more amorphous carbons.

Although the gases were not analysed in this work, when the conditioning catalyst was introduced, the production of  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{-C}_4$ ,  $\text{CO}$  was suggested to be increased. For example, when a 10 wt.%  $\text{Ni}/\text{Al}_2\text{O}_3$  was used for the gasification of polypropylene, 56.3 vol%  $\text{H}_2$ , 20 vol%  $\text{CO}$ , 9.3 vol%  $\text{CO}_2$ , 6.1 vol%  $\text{CH}_4$ , and 8.3 vol%  $\text{C}_2\text{-C}_4$  were reported [15]. The presence of hydrogen could provide a reducing environment for catalytic metals and hence prevent the poisoning of catalyst [16]. The growth of CNTs has been reported to be enhanced in a hydrogen atmosphere [17]. Cava et al. [18] reported that  $\text{H}_2$  had a ‘cleaning effect’ which could keep the active site of catalysts from encapsulating carbons. In addition, the increase of adding the amount of conditioning catalyst was suggested to increase hydrogen concentration in the carbon sources [19], which might be beneficial for the production of CNTs. It is to be noted that the conditioning catalyst might be deposited with coke. In this work, the reacted conditioning catalysts ( $\text{Ni}/\text{Al}_2\text{O}_3$ ) were not analysed, as the main objectives of this work was to study the  $\text{Ni}/\text{AAO}$  catalyst for the growth of CNTs.

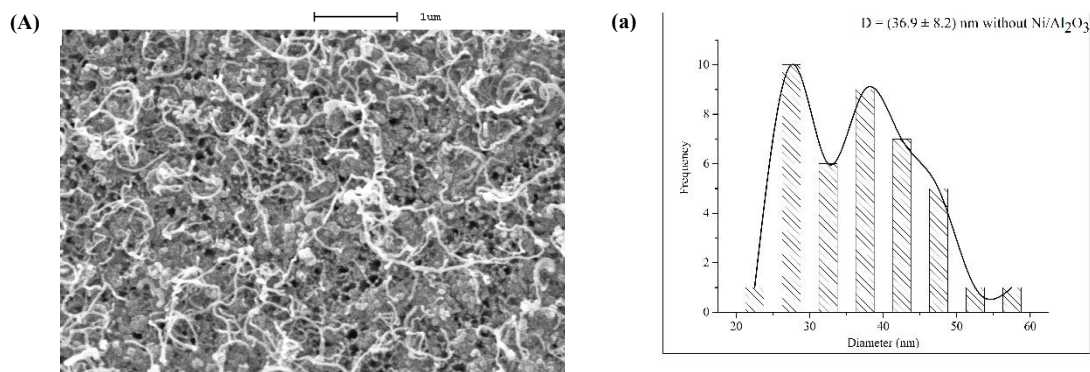
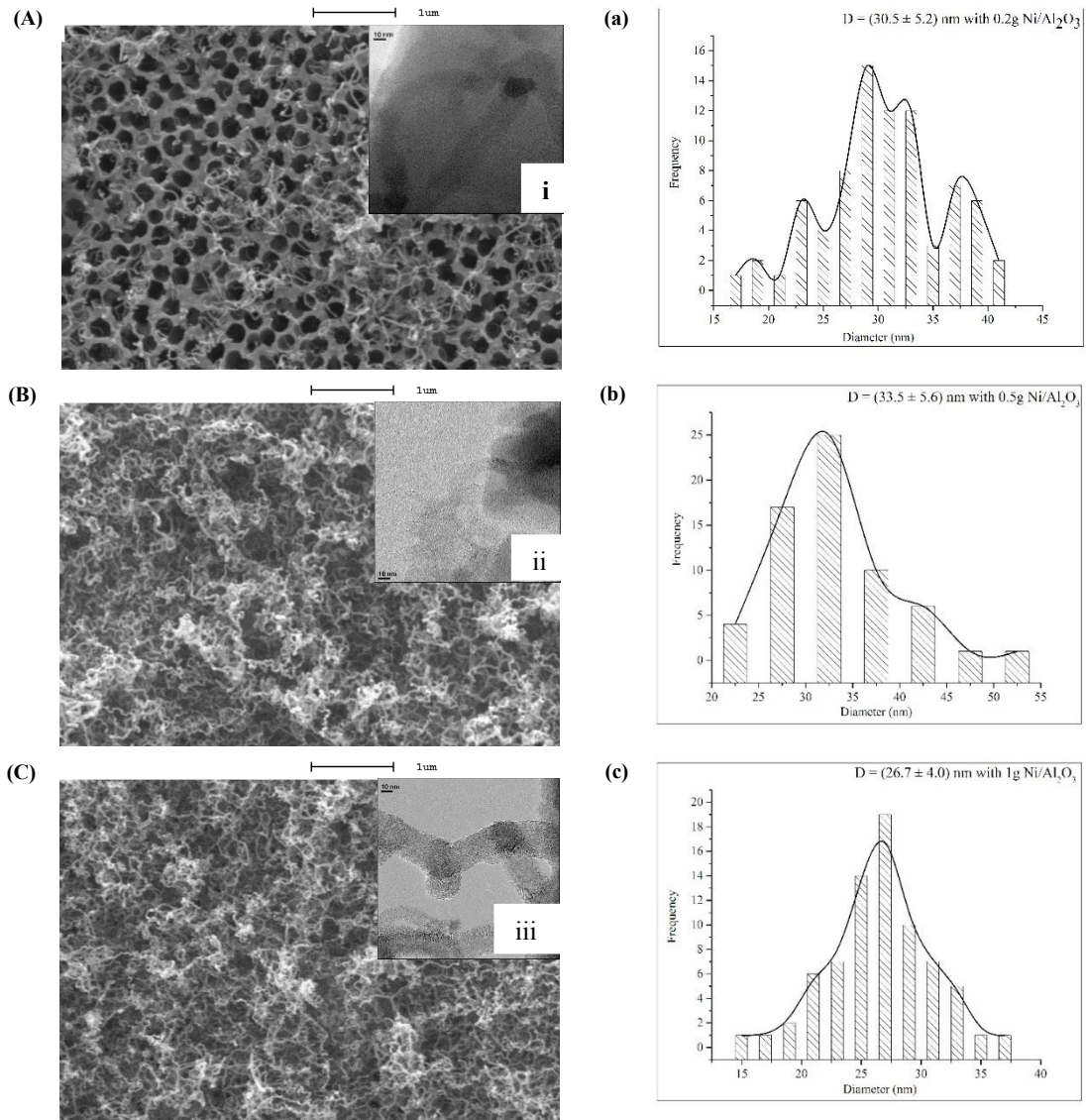
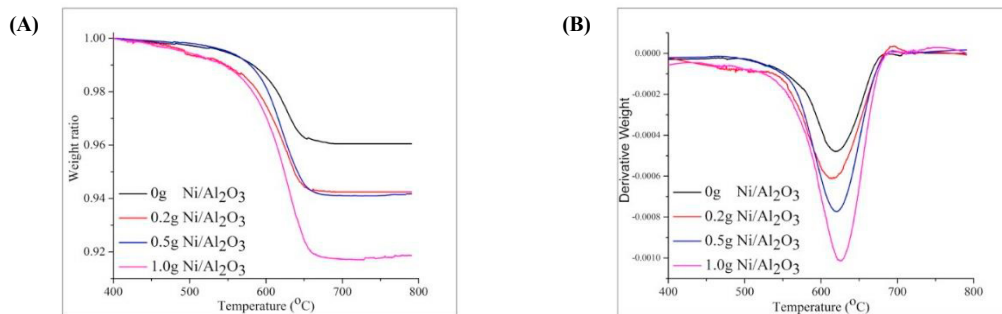


Fig. 2. SEM and diameter distribution results of CNTs formation using 0.1AAO without conditioning catalyst.



**Fig. 3.** SEM results for CNTs formation on 0.1AAO membrane with 0.2, 0.5, and 1 g Ni/Al<sub>2</sub>O<sub>3</sub> conditioning catalysts on the top (A-C), relevant diameter distribution (a-c) of CNTs (with TEM result i-iii).



**Fig. 4.** TGA-TPO (A) and DTG-TPO (B) results for the reacted catalysts obtained using different amounts of conditioning catalysts



#### 4. Conclusion

Carbon nanotubes (CNTs) were successfully produced from waste plastics using anodic aluminum oxide (AAO) membrane based catalyst. The addition of a conditioning catalyst prior to the formation of CNTs on the Ni/AAO catalyst was found to be beneficial. The quality of the produced CNTs in relation to the uniformity was enhanced when more conditioning catalyst was introduced in the process.

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